

主 論 文 要 旨

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論文題名

Supramolecular Assemblies of Anion-Responsive π -Conjugated Molecules

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主論文要旨

Appropriate arrangement of negatively charged species would afford dimension-controlled supramolecular assemblies. Planar anions, which are suitable for formation of stacking assemblies, can be prepared by anion complexation of π -conjugated planar anion receptors. However, most of the anion receptors previously reported were prepared in order to exhibit high anion-binding affinities and selectivities. Among various anion receptors, BF_2 complexes of dipyrrolyldiketones show efficient anion-binding properties by pyrrole inversion, and form planar receptor–anion complexes. Therefore, various anion-driven supramolecular structures can be fabricated based on planar receptor molecules and their receptor–anion complexes. During the course of PhD, modification (introduction of aryl rings) of the anion-responsive π -conjugated molecules and formation of supramolecular structures have been investigated.

As for receptor modification, two synthetic protocols have been examined: (i) preparation of aryl-substituted receptors from arylpyrroles and (ii) cross-coupling reaction of iodinated receptor molecules and aryl-boronic acids. Using protocol (i), various receptors including those bearing aliphatic chains were obtained, resulting in the formation of supramolecular gel from hydrocarbon solvents. Interestingly, anion-induced gel decomposition was observed due to the formation of ion-pairs of receptor–anion complexes with bulky cations. In contrast, introduction of planar cation salts fabricated supramolecular gel composed of nanoscale fibers from alternate stacking of planar charged species, namely “charge-by-charge assembly”. Further, the charge-by-charge assembly provided liquid crystal, whose structures were elucidated by synchrotron X-ray analysis. In addition, various anion receptor oligomers, which were prepared using protocol (ii), showed anion-driven helical structures in solution state as well as in the solid state. With the presence of Cl^- as a template, iodinated dimer can be transformed to receptor macrocycle, which exhibits an extremely high binding ability for Cl^- .